

PROCESS FOR THE PRODUCTION OF BIOLOGICALLY DEGRADABLE
ALIPHATIC POLYESTER AMIDE SOLUTIONS

The present invention concerns a method for the manufacture of solutions of biodegradable plastics, in particular of aliphatic polyester amides, and the use of the resulting solution for the manufacture of films and the coating of substrates made of metal, paper, wood, plastic, ceramic, and foodstuffs.

Plastics are widely used in households, commerce, and industry, for example as shaped elements, films, and coatings. Disposal thereof after use, however, represents an increasing problem. In recent years, biodegradable plastics have therefore also been developed.

Polyester amides based on natural amino acids are known from Polym. Bull. 28 (1992) 301-307. They are manufactured by way of a complex protective-group technique, since natural amino acids in combination with hydroxycarboxylic acids are generally involved; this is very cumbersome. In addition, these polymers have absolutely no mechanical properties which are necessary for the manufacture of useful objects.

Further biodegradable polyester amides made of lactic acid, diamines, and dicarboxylic acid dichlorides are disclosed in US Patents 4,343,931 and 4,529,792. Japanese Patents 79 113 593 and 79 109 594 disclose biodegradable polymers made from caprolactone and caprolactam. The polyester amides just mentioned are, however, complex to manufacture.

A further polyester amide is disclosed in European Patent Application EP 641 817. The polyester amide described therein can be processed thermoplastically, and is biodegradable. It has a melting point of at least 75°C, and the weight proportion of the ester structures is between 30 and 70%, and the proportion of amide structures between 70 and 30%. The aforesaid polymer has good mechanical properties, but processability is very difficult. Shaped elements can be manufactured from the polymer only in the mass. Solutions, for example in ethanol, are not stable, and quickly result in decomposition of the polymer.

It is the object of the present invention to manufacture solutions of biodegradable polyester amides so as to impart simplified and improved processability to them.

The subject matter of the present invention is a method for manufacturing solutions of biodegradable plastics, in particular of aliphatic polyester amides, which is
5 characterized in that the aliphatic polyester amide is added to a solvent mixture containing

- A) a C1-C4 alcohol;
- B) a C1-C6 ketone; and/or
- C) an aromatic carboxylic acid or a salt thereof.

10 It has been found, surprisingly, that biodegradable aliphatic polyester amides can be readily dissolved in the solvent mixture according to the present invention which contains components A, B and/or C. After only a few minutes, the polymer swells in the solution and dissolves. The dissolution rate can optionally be increased by mechanical actions such as agitation.

15 The resulting solution is stable for several days with no observable decomposition of the polymer structure.

According to a preferred embodiment, the method comprises the following steps:

- a) the plastic is placed in a vessel;
- b) the solvent mixture is added to the vessel until the plastic is covered by the
20 solvent mixture;
- c) the vessel is sealed and the plastic and solvent mixture are allowed to stand until the plastic has softened and swollen;
- d) the softened and swollen plastic is mechanically comminuted and the resulting emulsion is preferably filtered.

25 During the swelling operation, it may be advantageous to add further solvent in order to accelerate the swelling operation or effect further swelling of the plastic, if the

solvent mixture originally added to the vessel has been completely absorbed by the plastic.

In order to increase the absorption surface area of the plastic in this context, it may be opportune to comminute the plastic mechanically during the swelling operation so as thereby to accelerate the process.

In order to obtain a clear solution, the softened and swollen plastic is preferably filtered; the filtered-out solids can be added to a new batch of plastic + solvent mixture.

According to an alternative embodiment, powdered plastic is introduced into the solvent with continuous agitation, so that it dissolves immediately and a coating can be made.

Methanol and/or ethanol are preferably used as the C1-C4 alcohols of component A; it is preferred for environmental reasons to use methanol and ethanol obtained from plant-based raw materials. The solvent mixture contains the C1-C4 alcohol preferably in a quantity of 70 to 98.9 wt%, in particular in a quantity of 90 to 98.9 wt%.

Acetone and butanone (methyl ethyl ketone) have proven particularly suitable as the C1-C6 ketone. The ketone is present in the solvent preferably in a quantity from 0.1 to 5 wt%, preferably from 0.1 to 2 wt%.

Benzoic acid and its derivatives, i.e. compounds in which the aromatic ring is the substituent, have proven particularly successful as aromatic carboxylic acids. Benzoates are preferably used, denatonium benzoate being particularly preferred. Component C is usually present in the solvent mixture in a quantity of 0.01 to 5 ppm.

One polyester amide that is preferably used is made up of aliphatic monomers in which the weight proportion of the ester structure is between 30 and 70% and the proportion of the amide structure is between 70 and 30%. To allow the polymer to be used outdoors, i.e. even in sunlight, the polyester amide should have a melting point of at least 75°C.

Polyester amides that have proven suitable are, in particular, those described in

European Patent Application EP 0 641 817.

The average molecular weight (HW as determined by gel chromatography in n-cresol against a polystyrene standard) is from 10,000 to 300,000, preferably 20,000 to 150,000.

5 The polyester amides preferably used can be obtained in a manner known per se, for example by mixing the amide-forming and ester-forming starting components and then polymerizing them. Synthesis can also be accomplished by the "polyamide" method by stoichiometrically mixing the starting components, optionally with the addition of water and subsequent removal of water from the reaction mixture; and by the "polyester" method, by adding an excess of diol with branching of the acid groups, following by
10 rebranching or reamidization of those esters. In the second variant method, excess glycol is also distilled off in the water.

 The ester and amide segments are arranged purely statistically, governed fundamentally by the synthesis conditions. It is also possible, however, to use polyester
15 amides in which the monomers are distributed as longer segments in the polymer molecule.

 The following are used, for example, as monomers for the manufacture of the polyester amides which are preferably used:

 Dialcohols such as ethylene glycol, 1,4-butanediol, 1,3-butanediol,
20 1,6-hexanediol, diethylene glycol, etc.; and/or dicarboxylic acids such as oxalic acid, succinic acid, adipic acid and their lower alkyl esters; and/or hydroxycarboxylic acids and lactones, such as caprolactone, etc.; and/or amino alcohols such as ethanolamine, propanolamine, etc.; and/or cyclic lactams such as α -caprolactam and lauro lactam; and/or
 γ -amino carboxylic acids such as aminocaproic acid, etc.; and/or mixtures (1:1 salts) of
25 dicarboxylic acids such as adipic acid, succinic acid, etc. and diamines such as hexamethylenediamine, diaminobutane, etc.

 Hydroxyl- or acid-terminated polyesters having molecular weights between 200

and 10,000 can also be used as the ester-forming component.

The resulting polyester amides can also contain 0.1 to 5 wt%, preferably 0.1 to 2 wt%, of so-called branching agents. Compounds of this kind can be, for example, trifunctional alcohols such as trimethylolpropane or glycerol, tetrafunctional alcohols such as pentaerythrite, trifunctional carboxylic acids such as citric acid. Incorporation of such components increases the melt viscosity of the polyester amides. The biodegradability of these materials is not, however, impeded.

The solvent mixture used according to the present invention can additionally contain, as well as the aforementioned components A, B, and C, further constituents which improve the solubility of the polymers and may stabilize the solution. The mixture can also contain water in a quantity up to 30 wt%, preferably between 0.1 and 10 wt%.

The films manufactured according to the present invention offer a much wider application spectrum for biodegradable polyester amides than the pure substances.

For example, it is possible to cast films from the solutions. Clear, elastic films are obtained, which can be manufactured in any desired thickness and can be used, for example, as compostable trash bags or milk films.

The films can contain any desired fillers; care should be taken that the compostability of the polymers is not impaired by such additives. Examples of fillers are talc, CaSO_4 (for example, gypsum which is produced by flue gas desulfuration), compost, peat, garden mold, etc. The last-named fillers in particular make it possible to use the biodegradable polymers in agriculture and horticulture.

A further possible application of the solution obtained according to the present invention is utilization for coating substrates made of metal, paper, wood, plastic, ceramic, and foodstuffs. One possibility is use as a protective coating for metal substrates and glass as a protective coating during transport. In addition, for example, paper or board can be coated, so that the mechanical properties of board and paper and their resistance to moisture and water are enhanced, but the paper can be environmentally recycled after use. Coating can be accomplished, for example, with a dip method, by brush application, or

with a spray method. The films formed in each case can be pulled off in their entirety very quickly and without leaving a residue.

A further application of the solutions obtained according to the present invention is as an adhesive. For this, the solutions in concentrated form are applied onto the surfaces or points to be joined, and the surfaces are pressed together after a short exposure time which allows the solvent mixture to evaporate.

Example 1:

10 g of the polymer was placed in a beaker. 300 ml of a solvent mixture comprising 94 wt% ethyl alcohol, 2 wt% methyl ethyl ketone, 0.1 wt% denatonium benzoate, and water to make 100%, was added thereto and allowed to stand for three days. Swelling of the polymer was observed after a few hours. After two days the polymer was completely dissolved, yielding a clear, low-viscosity solution.

The polymer used was BAK 1095 (commercial product of Bayer AG, Leverkusen). BAK 2195 can also be used.

15 Example 2:

300 g of the polymer was placed in a beaker. The solvent mixture was added and was allowed to stand for 24 hours without heat, in a sealed vessel in which a vacuum had been drawn, until an increase in volume and a color change in the plastic had been noted.

The plastic was again covered with solvent, and then allowed to stand for approximately 24 hours in the sealed beaker.

20 This operation was repeated until an approximately threefold increase in volume had been noted, and the plastic was almost clear. The surface of the plastic was then sufficiently soft that mechanical comminution with a simple stirrer was possible. This operation was also repeated several times, further solvent being added as necessary for

dilution, until a low-viscosity solution was obtained. This was pressed through a fine-mesh filter to remove the solids still present in the emulsion.

The plastic used was BAK 1095. BAK 2195 can also be used.